EXECUTIVE SUMMARY

The motivation for this Nationwide Disinfection By-product (DBP) Occurrence Study was two-fold: First, more than 500 DBPs have been reported in the literature, yet there is almost no quantitative occurrence information for most. As a result, there is significant uncertainty over the identity and levels of DBPs that people are exposed to in their drinking water. Second, only a limited number of DBPs have been studied for adverse health effects. So, it is not known whether other DBPs (besides the few that are currently regulated) pose a risk to human health. To determine whether other DBPs pose an adverse health risk, more comprehensive quantitative occurrence and toxicity data are needed.

Because health effects studies are very expensive, it is not possible to test all DBPs that have been reported. It is also not feasible to measure >500 DBPs in waters across the United States. Thus, results of a DBP prioritization effort by scientists at the U.S. Environmental Protection Agency (USEPA) Office of Water and the USEPA Office of Prevention, Pesticides, and Toxic Substances were used to focus this study on those DBPs that were the most toxicologically significant. These EPA experts applied an in-depth mechanism-based structural activity relationship analysis to the more than 500 DBPs reported in the literature, supplemented by an extensive literature search for genotoxicity and other data, and ranked the carcinogenic potential of these DBPs. Approximately 50 DBPs that received the highest ranking for potential toxicity and that were not included in the USEPA's Information Collection Rule (ICR) were selected for this occurrence study. These DBPs, denoted as 'high priority' DBPs in this report, included such compounds as MX [3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone], brominated forms of MX (BMXs), halonitromethanes, iodo-trihalomethanes, and many brominated species of halomethanes, haloacetonitriles, haloketones, and haloamides.

For this Nationwide Occurrence Study, scientists from the USEPA's National Exposure Research Laboratory (NERL) initiated a collaboration with scientists at the University of North Carolina (UNC, Howard Weinberg, PI) and the Metropolitan Water District of Southern California (MWDSC, Stuart Krasner, co-PI). The 'high priority' DBPs, along with regulated and Information Collection Rule DBPs for comparison, were quantified in drinking waters across the United States. These waters represented diverse geographic regions with different source water quality. Several source waters contained relatively high bromide levels (where brominated DBPs would be expected to form). In addition, many of the waters selected for study were relatively high in total organic carbon (TOC). Waters treated with all four major disinfectants (chlorine, chloramines, ozone, and chlorine dioxide) were studied. In addition, the fate and transport of these DBPs was studied in the real distribution systems and in simulated distribution system (SDS) tests. Prior to this study, there was almost nothing known about the stability of these DBPs in the distribution system.

Because no quantitative analytical methods existed for most of the high priority DBPs, optimized analytical methods were initially developed at UNC and MWDSC. No one single analytical method could be used for all DBPs, so different methods were developed and optimized for specific groups of DBPs. Also, because there were no commercially available standards for many of these compounds, many had to be synthesized.

Another goal of this project was to use this opportunity to look for other DBPs that have not been previously identified in order to provide a more complete assessment of DBPs formed by different treatments in different regions of the United States. This work was carried out at the USEPA NERL-Athens laboratory. For this research, a combination of advanced mass spectrometric tools was used to identify the new DBPs.

Results revealed the presence of many of the high priority DBPs in the waters sampled. Important observations included finding the highest levels of iodo-trihalomethanes (THMs) at a plant that used chloramination without pre-chlorination. Levels of individual iodo-THMs ranged from 0.2 to 15 µg/L. Another important observation involved finding the highest concentration of dichloroacetaldehyde at a plant that used chloramine and ozone disinfection. Therefore, although the use of alternative disinfectants minimized the formation of the four regulated THMs, certain dihalogenated DBPs and iodo-THMs were formed at significantly higher levels than in waters treated with chlorine. Thus, the formation and control of the four regulated THMs is not necessarily an indicator of the formation and control of other halogenated DBPs, and the use of alternative disinfectants does not necessarily control the formation of all halogenated DBPs, and can even result in increased concentrations of some. Moreover, many of these halogenated DBPs—including certain dihalogenated and brominated species—were not studied in the ICR.

Halogenated furanones, including MX and brominated MX (BMX) analogues, were widely observed in these samplings. Another finding was the high levels of MX and MX-analogues in many samples. It was previously observed that MX did not exceed a concentration of 60 to 90 ng/L (the few measurements that had been conducted generally showed levels <60 ng/L). In this study, however, MX was often observed at levels significantly greater than 100 ng/L, with a maximum level of 310 ng/L observed in finished water from a treatment plant that disinfected a high-TOC water with chlorine dioxide, chlorine, and chloramines. These findings are significant because the levels of MX are much higher than previously reported. Likewise, several other analogues of MX were identified, including BMX analogues. Results include 170 ng/L and 200 ng/L levels for BMX-1 and BEMX-3, respectively (at a treatment plant that disinfected a high-bromide water with chlorine dioxide, chlorine, and chloramines). It is interesting that the drinking water utilities with the highest MX and BMX levels were from treatment plants that use chlorine dioxide for primary disinfection. MX did not form from chlorine dioxide disinfection *per se*, rather chlorine dioxide oxidation appeared to not destroy MX precursors (as ozone, another alternative disinfectant, does). Thus, MX and BMX formation was highest at treatment plants with high levels of TOC and bromide, respectively.

Halonitromethanes, including dihalogenated and brominated species not included in the ICR, were found in some of the samples; levels of individual species ranged from 0.1 to 3 µg/L. In some cases, pre-ozonation was found to increase the formation of the trihalonitromethanes (brominated analogues of chloropicrin [trichloronitromethane]). Many brominated acids were also identified in several finished waters that contained elevated levels of bromide in their source waters. A number of brominated acids were identified for the first time (i.e., brominated propanoic, propenoic, butanoic, butenoic, oxopentanoic, heptanoic, nonanoic, and butenedioic acids), with most being observed in the finished water from a treatment plant that has significant bromide levels in its source water. One of the high priority DBPs, 3,3-dichloropropenoic acid, was found in several finished waters, giving further evidence that haloacids with longer carbon chains are prevalent DBPs (i.e., haloacetic acids are not the only haloacids formed during disinfection).

Dihaloacetaldehydes and brominated analogues of chloral hydrate (trichloroacetaldehyde) were detected in many samples, as were mono-, di-, tri-, and/or tetra-species of halomethanes and haloketones. Several haloamides were also found in finished waters at levels similar to DBPs that are commonly measured (low µg/L levels). This is a class of DBPs that has not been previously quantified, but the levels observed in this study indicate that their levels in finished waters are not trivial. In addition, carbon tetrachloride was detected in some of the waters measured, with a maximum of 0.8 µg/L observed. Although carbon tetrachloride was present in sampled finished drinking waters, its identity as a DBP could not be proven, since carbon tetrachloride is sometimes used to clean out chlorine cylinders before they are filled. Thus, it could be either a DBP or a contaminant from the cleaning process.

Another finding in this study was the discovery of iodoacids for the first time. Five new iodoacid species were tentatively identified: iodoacetic acid, iodobromoacetic acid, iodobromopropenoic acid (2 isomers), and 2-iodo-3-methylbutenedioic acid. High resolution mass spectrometry confirmed the presence of iodine in their structures and the overall empirical formulas for these new DBPs. One of these—iodoacetic acid—has been confirmed through the analysis of an authentic chemical standard (match of retention time and mass spectrum). Additional synthetic standards are currently being prepared to confirm the other iodoacid identifications. These iodoacids were observed as DBPs in a high-bromide water from a treatment plant that uses only chloramine disinfection. Another iodinated DBP, tentatively identified as iodobutanal, was found in finished waters from treatment plants on both coasts that can be impacted by saltwater intrusion (sea water is a source of iodide in addition to a major source of bromide in some drinking waters). This DBP has also not been reported previously.

In addition to the new iodinated DBPs and new brominated acids, another brominated ketone was identified for the first time: 1-bromo-1,3,3-trichloropropanone, which was found in many of the waters sampled.

The stability of DBPs in actual distribution systems and in simulated distribution system (SDS) tests varied. In most cases where chloramination was used, the DBPs were relatively stable. However, when free chlorine was used, THMs and other DBPs, including haloacetic acids, increased in concentration both in the actual distribution system and in SDS tests. Haloacetonitriles generally were stable (at the distribution-system pH levels encountered in this study) and increased in concentration, but many of the haloketones were found to degrade in the distribution system and SDS tests. Halonitromethanes and dihaloacetaldehydes were found to be stable in these systems and tests. Although controlled laboratory studies had suggested instability of halogenated furanones, particularly MX, in water, MX and MX-analogues were sometimes stable, and sometimes they degraded somewhat in the distribution systems and SDS tests. When the MX analogues showed some degradation in the distribution system, they were generally still present at detectable levels, indicating that they do not completely degrade in the distribution system. Many times, the BMXs were stable.